REE DIFFUSIVITIES IN MELILITE: A PRELIMINARY STUDY USING THE SIMS DEPTH PROFILE METHOD.

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Introduction. Diffusivities of the rare earth elements (REE), La, Pr, Tb and Tm, have been measured for synthetic single crystal of melilite (Âkermanite, $Ca_2MgSi_2O_7$) using depth profile method by secondary ion mass spectrometry (SIMS), for the purpose of confirming the possible diffusive fractionation of REE in the Allende CAI's etc [1,2].

In our previous works [3, 4] we have measured the diffusivities of divalent cations and REE (Gd, Tm, and Sc) in Âkermanite using radioactive tracers. However, tracer experiment is limited by availability of radioactive isotopes with half-lives and -ray energies which are adequate for diffusion measurement. By using SIMS any REE can be measured in principle, unless an oxide ion interferes measurement of metal ion with the same mass number. In addition, SIMS has higher spatial resolution of a few nm rather than µm in tracer experiment or EPMA.

Experimental. The synthetic single crystal of melilite (Âkermanite, $Ca_2MgSi_2O_7$) was grown by the Czochralski method. The conditions of growing melilite were the same as our previous works [3,4]. The single crystal of melilite was cut into small slabs with a 5 mm square surface perpendicular to the c-axis and 1 mm in thickness by a diamond saw. The surface of the slabs was polished with ~0.25 µm diamond paste and finished with 0.05 µm alumina paste to obtain necessary flatness of the surface. After polishing, the melilite samples were coated with a thin evaporated films (~200 Å) of REE oxide. The samples were annealed in air in a resistance furnace from 20 min (1200°C) to 80 hours (1100°C).

The diffusion profiles of individual REE, secondary ion intensities versus penetration distance into the annealed samples, were determined by SIMS (IMS-3f, Cameca, Paris, France) using depth profile method at Tokyo Institute of Technology.

The primary ion beam was massfiltered negative [16]O accelerated to 12.5 keV with beam current of 60 to 100 nA and beam spot size of 50 to 80 µm diameter. The primary ion beam was rastered about 300 to 400 µm square during beam irradiation. Electrostatic charging on the samples by the primary ion beam was virtually eliminated by 25 nm of gold film evaporated on the sample surface. The intensities of the positive secondary ions were measured by offsetting the sample accelerating voltage (-60 V) and the energy band-pass was set to 20 eV.

The secondary ions were collected from the central area of sample surface (60 µm diameter) using a mechanical aperture in order to minimize artifacts arising from crater edge effects and redeposition of materials. Counts of secondary ions measured are [30]Si, [42]Ca, [139]La, [141]Pr, [159]Tb, [169]Tm. Secondary ion intensities of individual REE in melilite as a function of penetration distance is shown Fig.1a and b.

The final crater depth was measured using an optical interferometer.

Results & Discussion. Depth profiles obtained by SIMS measurement shown in Fig.1a and b satisfy the conditions for thin film diffusion model. Diffusion coefficients of individual REE were calculated by the best fit to the theoretical depth profiles obtained as the solution of the Fickian diffusion equations [5].

$$c(x) = (M/\sqrt{4\pi Dt}) \exp(-x^2/4Dt) \quad (1)$$

where $c(x)$ is the concentration at a depth x, M is the total amount of source of diffusion, D is the diffusion coefficient, t is the duration of the anneal. According to equation (1), the decrease of the Log (REE intensities / [30]Si intensities) from a depth profile should yield a linear array. A slope equal to $1/(4Dt)$ was computed by least-square fitting and diffusion coefficient was calculated. The solution of the diffusion equation for thin film is reasonable for the measuring data.

The calculating results of diffusivities of individual REE in melilite at 1200°C and 1100°C are summarized in Table 1. The diffusivities observed at 1200°C show increasing trend from La to Tm by a factor of about 30, which is parallel to that observed by the previous work [3] (Fig.2). However, diffusivities observed at 1100°C are almost similar and 2 to 4 orders of magnitude lower compared with the results at 1200°C.

The observed large differences in D's observed at 1200°C and 1100°C result in unusually large activation energy (E_D) values of ca. 790 ~ 1600 kJ/mol, if the Arrhenius relationship which is typically defined as in equations (2) and are used to calculate E_D.

$$D = D_0 \exp(-E_D/RT) \quad (2)$$

where D is the diffusion coefficient, D_0 is the preexponential factor, E_D is the activation energy for diffusion, T is the absolute temperature (K) and R is the gas constant. The observed, unusually large activation energy values and the observed large differences in ionic size-dependence of diffusivity suggest the mechanisms for diffusion occurred at 1200°C and 1100°C are different.

Conclusions. It is found that depth profile method by SIMS provided adequate results of diffu-

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sivities of REE in Âkermanite at 1200°C, which are consistent with the previous works [3] ; i.e., diffusivities increase from La to Tm by a factor of about 30. The results suggest heterogeneous distribution of REE in the individual melilite grains in the Allende CAI's may have been affected by diffusional redistribution. However, experiments at 1100°C diffusivities are very low and similar for La, Pr, Tb and Tm. It is suggested that diffusion transport of REE occurred under a different mechanism in these experiments.

References: [1] Koike O. et al. (1994) LPS, **25**, 725-726. [2] Davis A.M. et al., (1996) LPS, **27**, 291-292. [3] Morioka M. and Nagasawa H., (1996) LPS, **27**, 907-908. [4] Morioka M. and Nagasawa H., (1991) GCA, **55**, 751-759. [5] Crank J. (1975) Oxford University Press.
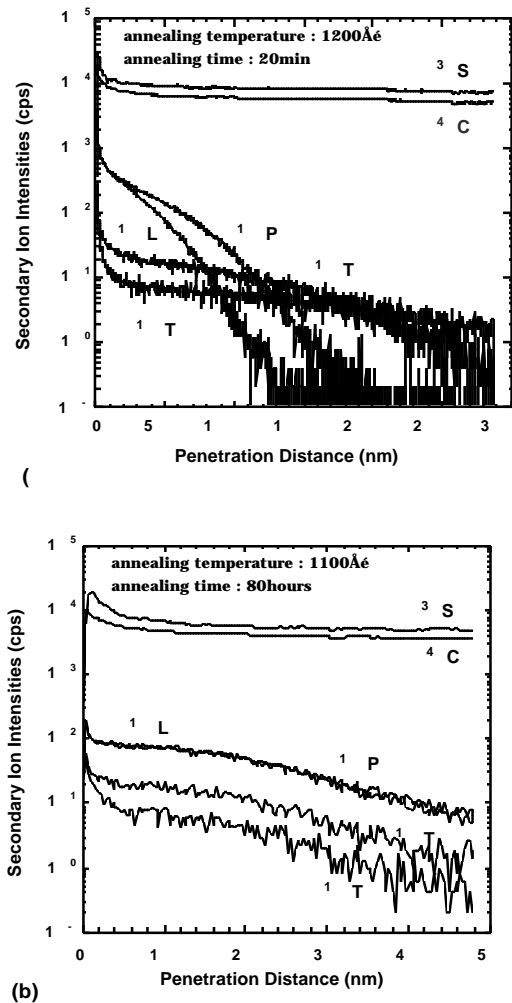
TABLE 1. Diffusion coefficients of individual REE in melilite at 1200°C and 1100°C.

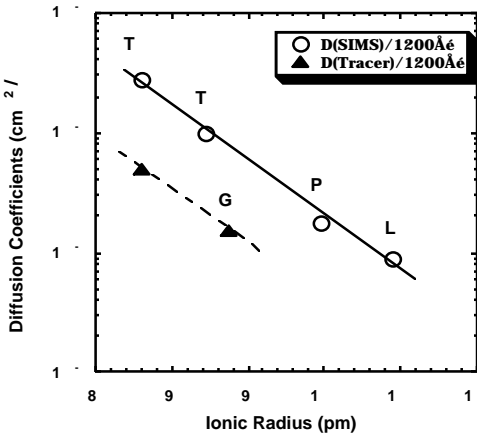| REE	1200°C [D (cm²/sec)]	1100°C [D (cm²/sec)]
La	8.90e-13	2.86e-15
Pr	1.80e-12	2.70e-15
Tb	9.98e-12	2.64e-15
Tm	2.70e-11	2.61e-15

Fig 2. Plot of diffusion coefficients against ionic radius of individual REE at 1200°C in melilite. The observed trend is parallel to that observed for tracer diffusion [3].
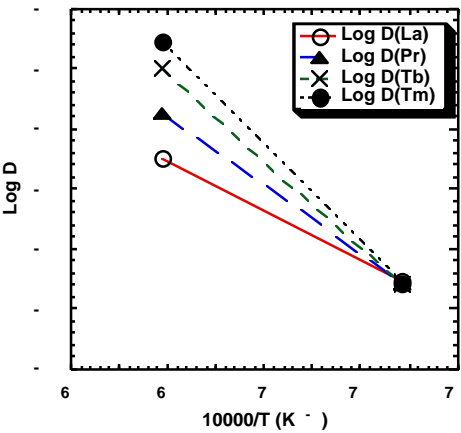

Fig 1. (**a**) Typical depth profile of REE diffusion in melilite at 1200°C and (**b**) at 1100°C.

Fig 3. Arrhenius plot of individual REE in melilite.

TABLE 2. Activation energy for individual REE in melilite.

REE	Activation Energy (kJ/mol)
La	790
Pr	1100
Tb	1400
Tm	1600